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Formation of Difluorosulfane Complexes of the Third Row Transition Metals by Sulfur-to-Metal Fluorine Migration in Trifluorosulfane Metal Complexes: The Anomaly of Trifluorosulfane Iridium Tricarbonyl

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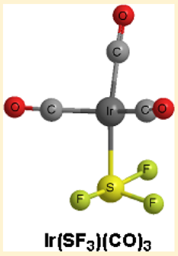
Supporting Information



Ir(SF$_3$)(CO)$_3$

ABSTRACT: The stability of the experimentally known complex $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ of the third row transition metal iridium suggests that SF_3 complexes of the third row transition metals might be viable species in contrast to the SF_3 complexes of the first row transition metals previously studied by theoretical methods. However, the metal complexes $[M](SF_3)$ ($[M]$ = $Ta(CO)_5$, $Re(CO)_4$, $CpW(CO)_2$, $CpOs(CO)$, and CpPt) containing three-electron donor tetrahedral SF_3 ligands are thermodynamically disfavored relative to the isomeric $[M](SF_2)(F)$ derivatives with predicted energy differences ranging from −19 to −44 kcal/mol. The one exception is an $Ir(SF_3)(CO)_3$ isomer containing a one-electron donor pseudo-square-pyramidal SF_3 ligand having essentially the same energy as the lowest energy $Ir(SF_2)(F)(CO)_3$ isomer. This, as well as the stability of the known $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, suggests that metal complexes containing one-electron donor pseudo-square-pyramidal SF_3 ligands might be viable synthetic objectives in contrast to those containing three-electron donor tetrahedral SF_3 ligands. The $[M](SF_2)(F)$ derivatives formed by sulfur-to-metal fluorine migration from isomeric $[M](SF_3)$ complexes are predicted to be viable toward SF_2 dissociation to give the corresponding $[M](F)$ derivatives. This suggests the possibility of synthesizing metal complexes of the difluorosulfane (SF_2) ligand via the corresponding metal trifluorosulfane complexes with the SF_3^+ cation as the ultimate source of the SF_2 ligand. Such a synthetic approach bypasses the need for the very unstable SF_2 as a synthetic reagent.

1. INTRODUCTION

The chemistry of strong π-acceptor ligands is an important area of coordination chemistry, particularly with respect to stabilization of low formal oxidation states. Carbon monoxide is the prototypical strong π-acceptor ligand in the thousands of known metal carbonyl derivatives. Trifluorophosphine (PF_3) resembles carbon monoxide in being a similar strong π-acceptor ligand.[1−10] In fact, the homoleptic zerovalent metal derivatives, such as $Cr(PF_3)_6$, $Fe(PF_3)_5$, and $Ni(PF_3)_4$, are even more thermally and oxidatively stable than the corresponding homoleptic metal carbonyls.[11,12] This greater stability of zerovalent $M(PF_3)_n$ complexes relative to corresponding $M(CO)_n$ complexes has allowed the synthesis of some zerovalent metal trifluorophosphine complexes that do not have stable metal carbonyl analogues.

The nitrosonium ion, NO^+, is isoelectronic with carbon monoxide and is the basis for the extensive chemistry of metal nitrosyls.[13,14] The trifluorosulfonium ligand SF_3^+ ligand bears a similar relationship to the NO^+ ligand as the PF_3 ligand bears to the CO ligand. Furthermore, just as nitrosonium salts of weakly coordinating anions such as $[NO^+][BF_4^-]$ and $[NO^+][EF_6^-]$ (E = P, As, Sb) are stable species, so are the corresponding SF_3^+ salts[15] $[SF_3^+][BF_4^-]$, $[SF_3^+][EF_6^-]$ (E = P, As, Sb) stable species obtained by abstraction of fluoride from SF_4 with strongly Lewis acidic fluorides.[16]

A characteristic feature of metal nitrosyl chemistry is the dichotomy of the NO ligand in exhibiting either linear or bent M−N−O geometry (Figure 1). A linear neutral NO ligand acts as a formal three-electron donor ligand to a transition metal atom. Such a three-electron donor neutral NO ligand corresponds to the nitrosonium ion NO^+. However, a bent neutral NO group has a pseudotrigonal nitrogen atom with a stereochemically active lone pair and thus can only donate a single electron to the transition metal. Such a one-electron donor neutral NO ligand corresponds to the NO^- anion.

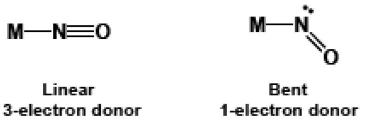


Figure 1. Comparison of a linear three-electron donor NO group with a bent one-electron donor NO group.

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A dichotomy between three-electron and one-electron donor neutral ligands similar to that in NO complexes (Figure 1) is possible in the chemistry of SF_3 metal complexes (Figure 2).

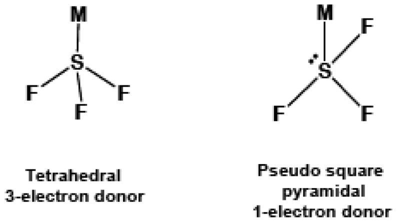


Figure 2. Comparison of a tetrahedral three-electron donor neutral SF_3 group with a pseudo-square-pyramidal one-electron donor neutral SF_3 group.

Thus, the neutral SF_3 ligand in an SF_3−M system with tetrahedral sulfur coordination can function as a three-electron donor to the transition metal. Such a three-electron donor neutral SF_3 ligand corresponds to the trifluorosulfonium cation SF_3^+. However, an SF_3 ligand with a stereochemically active lone pair is possible with pseudo-square-pyramidal sulfur coordination. Such a neutral SF_3 ligand can donate only a single electron to the transition metal and thus corresponds to the trifluorosulfate anion SF_3^-.

Despite the extensive chemistry of transition metal complexes of the CO, PF_3, and NO ligands, the apparently related metal complexes of the SF_3 ligand are almost unknown experimentally. Thus, the only well-documented example of a transition metal SF_3 complex in the literature is the iridium derivative[17] $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, which is obtained from the reaction of *trans*-$(Et_3P)_2Ir(CO)Cl$ with SF_4. The neutral SF_3 ligand in this iridium complex appears to have a pseudo-square-pyramidal sulfur atom and thus functions as a one-electron donor. This gives the central iridium atom in $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ the favored 18-electron configuration by receiving a pair of electrons from each of the two Et_3P ligands and the single CO ligand and single electrons from the Cl, F, and SF_3 ligands, all considered formally as neutral species. The analogous iridium nitrosyl compound $(Et_3P)_2Ir(CO)(NO)(Cl)(F)$ has not been reported.

The absence of known complexes containing three-electron donor SF_3 ligands analogous to the normal three-electron donor NO ligand raises the question as to whether such SF_3 complexes are indeed viable. In this connection a density functional theory study showed that the first-row transition metal complexes $M(SF_3)(CO)_n$ (M = V, $n = 5$; M = Mn, $n = 4$; M = Co, $n = 3$) and $CpM(SF_3)(CO)_n$ (Cp = η^5-C_5H_5; M = Cr, $n = 2$; M = Ni, $n = 0$) analogous to the known metal nitrosyl derivatives[18−21] $M(NO)(CO)_n$ and $CpM(NO)(CO)_n$ are strongly disfavored thermochemically relative to the corresponding $M(SF_2)(F)CO)_n$ and $CpM(SF_2)(F)CO)_n$ complexes arising from fluorine shift from sulfur to the transition metal.[22] In other words, the SF_3 ligand appears to be too strong a fluorinating agent for such first row transition metal carbonyl complexes to be viable. This is consistent with the use of sulfur−fluorine compounds, notably SF_4, as fluorinating agents, particularly in organic chemistry.[23]

The previous study[22] was mainly limited to first row transition metals. A question of interest is whether third row transition metal complexes might be more resistant toward fluorination by a pendant SF_3 ligand. Accordingly, the corresponding study was done using the third row transition metal complexes $M(SF_3)(CO)_n$ (M = Ta, $n = 5$; M = Re, $n = 4$; M = Ir, $n = 3$) and $CpM(SF_3)(CO)_n$ (Cp = η^5-C_5H_5: M = W, $n = 2$; M = Os, $n = 1$; M = Ni, $n = 0$). With one exception, the $[M](SF_3)$ complexes for these third row transition metals were found to be of much higher energies than the isomeric $[M](SF_2)(F)$ complexes similar to the situation with the previously studied[22] first row transition metals. The exception is the iridium carbonyl system where isomeric $Ir(SF_2)(F)(CO)_3$ and $Ir(SF_3)(CO)_3$ complexes have essentially the same energies. The low energy iridium complex $Ir(SF_3)(CO)_3$ has a one-electron donor pseudo-square-pyramidal sulfur atom with a stereochemically active lone pair thereby giving the iridium atom a 16-electron configuration rather than the favored 18-electron configuration. All of the other third row transition metal $[M](SF_3)$ complexes have three-electron donor SF_3 groups with tetrahedral sulfur atoms and thus lie at very high energies relative to isomeric $[M](SF_2)(F)$ complexes.

Another question of interest is the viability of the SF_2 metal complexes obtained from the SF_3 metal complexes by fluorine migration from sulfur to the metal atom. The chemistry of SF_2 metal complexes is of interest since SF_2 is a potentially strong π-acceptor ligand similar to PF_3. However, no transition metal SF_2 complexes have been synthesized, probably owing to the instability of free SF_2 except either in low temperature matrices[24] or highly diluted in the gas phase.[25,26] We demonstrate in this theoretical study that SF_2 metal complexes are potentially viable since the processes $[M](SF_2)(F) \rightarrow [M](F) + SF_2$ are all endothermic.

2. THEORETICAL METHODS

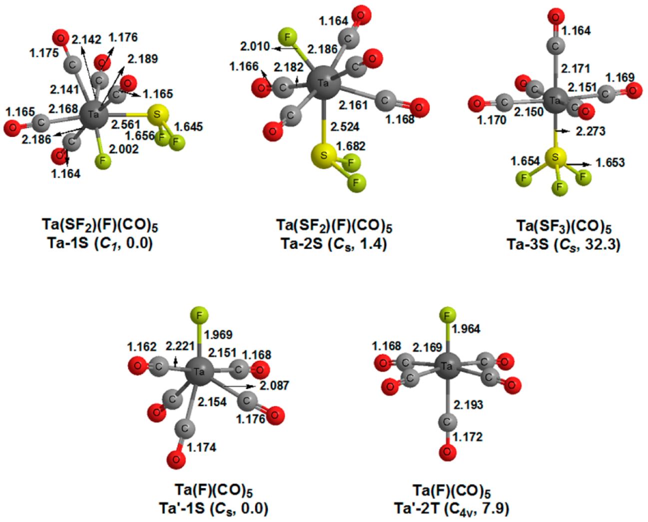
All calculations were performed using the Gaussian 09 program package.[27] Two density functional theory (DFT) methods were used, namely B3LYP and BP86. The B3LYP method is a hybrid HF-DFT method combining Becke's three parameter functional (B3)[28] with the Lee, Yang, and Parr (LYP)[29] correlation functional. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B)[30] with Perdew's 1986 correlation functional (P86).[31]

The double-ζ plus polarization (DZP) basis sets were used for all computations. For carbon, oxygen, fluorine, and sulfur, these DZP basis sets were obtained by adding one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.00$, $\alpha_d(S) = 0.70$, respectively, to the Huzinaga−Dunning standard contracted DZ sets, designated as (9s5p1d/4s2p1d).[32,33] For H, a set of p polarization functions ($\alpha_p(H) = 0.75$) was added to the Huzinaga−Dunning DZ sets. For the third row transition metals Ta, W, Re, Os, Ir, and Pt, basis sets with effective core potentials (ECPs) were used. In the present research we adopted the Stuttgart/Dresden double-ζ (SDD) ECP basis sets.[34] The harmonic vibrational frequencies were obtained at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The fine grid (75, 302) is the default for evaluating integrals numerically.[35] The finer grid (120, 974) was used for more precise resolution of the small imaginary vibrational frequencies. Unless otherwise indicated, all of the structures reported in this article were genuine minima, with only real vibrational frequencies. The tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

Structures are designated as **M-nS/T**, where M is the third row transition metal, **n** numbers the structures according to their relative energies (BP86 and B3LYP methods), and **S** (or **T**) represents singlet (or triplet) electronic state structures. For example, **Ta-1S** is the lowest-lying singlet structure for $Ta(SF_2)(F)(CO)_5$. In addition, the results obtained by the BP86 and B3LYP methods are consistent with each other. Therefore, only the BP86 results are discussed in this Article. The B3LYP results are presented in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. $Ta(SF_3)(CO)_5$ and $Ta(SF_2)(F)(CO)_5$ Derivatives. The two $Ta(SF_2)(F)(CO)_5$ structures **Ta-1S** and **Ta-2S** with separate SF_2 and F ligands are of lower energy than the $Ta(SF_3)(CO)_5$ structure **Ta-3S** with an intact SF_3 ligand (Figure 3). The Ta−S distances in **Ta-1S** and **Ta-2S** are predicted to be ∼2.6 and ∼2.5 Å, respectively. The structure **Ta-2S** lies only 1.4 kcal/mol above the global minimum $Ta(SF_2)(F)(CO)_5$ structure **Ta-1S**. The Ta−F distances are ∼2.0 Å in **Ta-1S** and **Ta-2S**. The SF_2 and CO ligands are two-electron donors, and the F atom is a one-electron donor leading to the favored 18-electron configuration for the tantalum atoms. Structures **Ta-1S** and **Ta-2S** differ only in the relative positions of the SF_2 and F ligands.



$Ta(SF_2)(F)(CO)_5$
Ta-1S (C_1, 0.0)

$Ta(SF_2)(F)(CO)_5$
Ta-2S (C_s, 1.4)

$Ta(SF_3)(CO)_5$
Ta-3S (C_s, 32.3)

$Ta(F)(CO)_5$
Ta'-1S (C_s, 0.0)

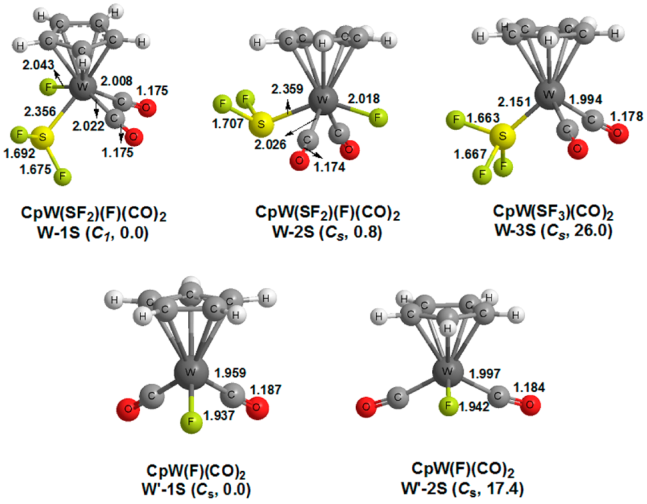
$Ta(F)(CO)_5$
Ta'-2T (C_{4v}, 7.9)

Figure 3. Optimized geometries (bond lengths in Å) at the BP86/DZP level of theory for the $Ta(SF_2)(F)(CO)_5$, $Ta(SF_3)(CO)_5$, and $Ta(F)(CO)_5$ structures. The numbers in parentheses are the relative energies (Δ*E* in kcal/mol). The subsequent figures have the same arrangement.

The only $Ta(SF_3)(CO)_5$ structure **Ta-3S** lies 32.3 kcal/mol above the lowest energy $Ta(SF_2)(F)(CO)_5$ structure **Ta-1S** (Figure 3). The SF_3 group in **Ta-3S** can be regarded as a three-electron donor thereby giving the tantalum atom in **Ta-3S** the favored 18-electron configuration.

The tantalum carbonyl fluoride $Ta(F)(CO)_5$ was also studied in order to investigate the thermodynamic stability of the structures $Ta(SF_2)(F)(CO)_5$ toward liberation of SF_2 to give the corresponding metal carbonyl fluoride. Two $Ta(F)(CO)_5$ structures were obtained (Figure 3). The lowest energy $Ta(F)(CO)_5$ structure **Ta′-1S** has highly distorted octahedral coordination with only C_s symmetry. However, the triplet $Ta(F)(CO)_5$ structure **Ta′-2T**, lying 7.9 kcal/mol in energy above **Ta′-1S**, has nearly ideal octahedral tantalum coordination with C_{4v} symmetry. The Ta−F distances in **Ta′-1S** and **Ta′-2T** of ∼1.97 Å are slightly shorter than those in $Ta(SF_2)(F)(CO)_5$.

3.2. $CpW(SF_3)(CO)_2$ and $CpW(SF_2)(F)(CO)_2$ Derivatives. Two $CpW(SF_2)(F)(CO)_2$ structures and one $CpW(SF_3)(CO)_2$ structure were found (Figure 4). The $CpW(SF_2)(F)(CO)_2$ structures, with separate F and SF_2 ligands, have lower energies than the $CpW(SF_3)(CO)_2$ isomer. Structures **W-1S** and **W-2S**, differing only by the orientation of the SF_2 and F groups, are nearly degenerate with **W-2S** lying only 0.8 kcal/mol above **W-1S**. The W−F and W−S distances in **W-1S** and **W-2S** are ∼2.0 and ∼2.3 Å, respectively. The SF_2 ligand is a two-electron donor, and the F atom is a one-electron donor leading to the favored 18-electron configuration for the tungsten atom. Structure **W-1S** has the SF_2 and F ligands in *cis* (lateral) positions whereas **W-2S** has the SF_2 and F ligands in *trans* (diagonal) positions.



$CpW(SF_2)(F)(CO)_2$
W-1S (C_1, 0.0)

$CpW(SF_2)(F)(CO)_2$
W-2S (C_s, 0.8)

$CpW(SF_3)(CO)_2$
W-3S (C_s, 26.0)

$CpW(F)(CO)_2$
W′-1S (C_s, 0.0)

$CpW(F)(CO)_2$
W′-2S (C_s, 17.4)

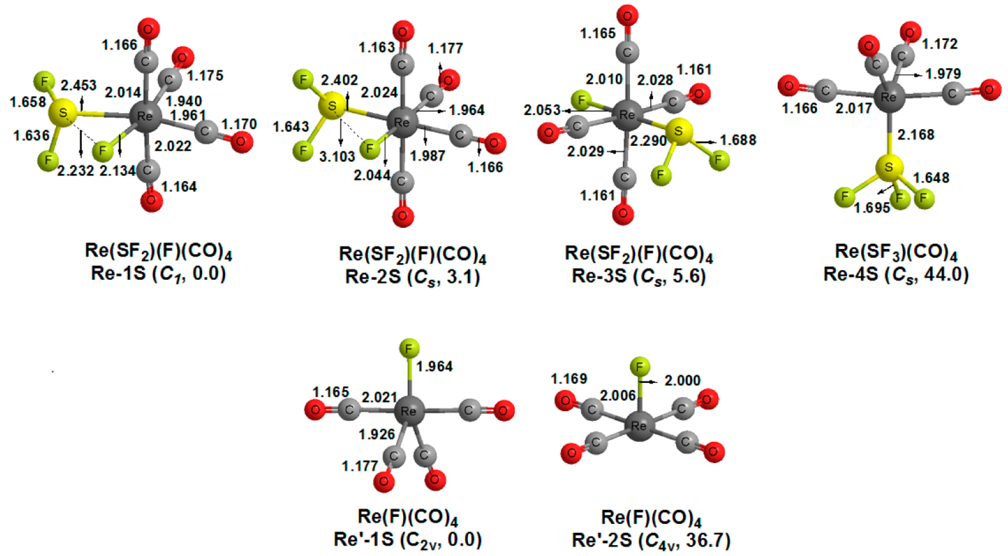
Figure 4. Optimized geometries for the $CpW(SF_2)(F)(CO)_2$, $CpW(SF_3)(CO)_2$, and $Cp(F)W(CO)_2$ structures.

The $CpW(SF_3)(CO)_2$ structure **W-3S** with an intact SF_3 group is a relatively high energy structure, lying 26.0 kcal/mol above **W-1S** (Figure 4). The W−S distance in **W-3S** of 2.151 Å is ∼0.2 Å shorter than the W−S distances in **W-1S** and **W-2S**. The SF_3 group in **W-3S** can be considered to be a three-electron donor, so that the tungsten atom in **W-3S**, like those in **W-1S** and **W-2S**, has the favored 18-electron configuration.

Two geometrically similar $CpW(F)(CO)_2$ structures with C_s symmetry were obtained for the corresponding metal carbonyl fluoride differing only in the C−W−C angle between the CO groups (Figure 4). Thus, the lower energy $CpW(F)(CO)_2$ structure **W′-1S** has an acute C−W−C angle of 72.6°, whereas the C−W−C angle in **W′-2S** is obtuse at 108.3°. This major difference in the C−W−C angle has a substantial effect on the energy since **W′-2S** lies 17.4 kcal/mol above **W′-1S**. The W−F distances in **W′-1S** and **W′-2S** of ∼1.94 Å are slightly shorter than those in the $CpW(SF_2)(F)(CO)_2$ structures.

3.3. $Re(SF_3)(CO)_4$ and $Re(SF_2)(F)(CO)_4$ Derivatives. The $Re(SF_2)(F)(CO)_4$ structures, with separate F and SF_2 ligands, also have significantly lower energies than their $Re(SF_3)(CO)_4$ isomer. Three $Re(SF_2)(F)(CO)_4$ structures were found (Figure 5). The $Re(SF_2)(F)(CO)_4$ structures **Re-1S** and **Re-2S** are both *cis* isomers. The lower energy structure **Re-1S** has the fluorine ligand bridging the Re−S bond with an S−F distance of 2.232 Å and an Re−F distance of 2.134 Å. However, in the higher energy structure **Re-2S**, lying 3.1 kcal/mol above **Re-1S**, the fluorine ligand is clearly a truly terminal ligand with a nonbonding S···F distance of 3.103 Å.

The $Re(SF_2)(F)(CO)_4$ structure **Re-3S**, lying 5.6 kcal/mol in energy above **Re-1S**, is closely related to **Re-1S** and **Re-2S** except the SF_2 and F ligands are in *trans* rather than *cis* positions (Figure 5). The Re−S distance of ∼2.3 Å in **Re-3S** is ∼0.2 Å shorter than the Re−S distances in **Re-1S** and **Re-2S** owing to the weaker *trans* effect of fluorine relative to CO. The



$Re(SF_2)(F)(CO)_4$
Re-1S (C_1, 0.0)

$Re(SF_2)(F)(CO)_4$
Re-2S (C_s, 3.1)

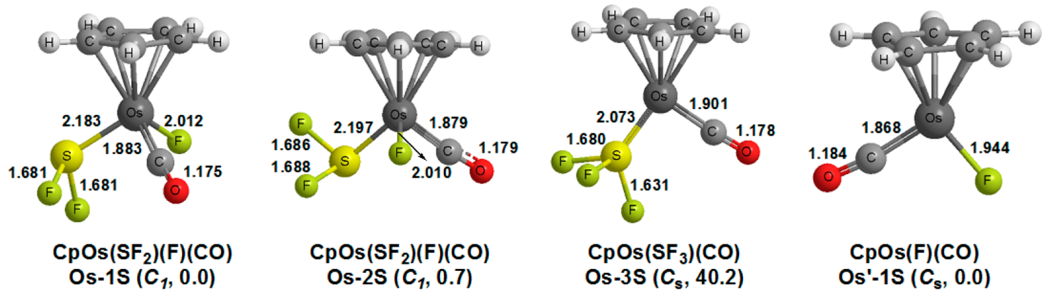
$Re(SF_2)(F)(CO)_4$
Re-3S (C_s, 5.6)

$Re(SF_3)(CO)_4$
Re-4S (C_s, 44.0)

$Re(F)(CO)_4$
Re'-1S (C_{2v}, 0.0)

$Re(F)(CO)_4$
Re'-2S (C_{4v}, 36.7)

Figure 5. Optimized geometries for the $Re(SF_2)(F)(CO)_4$, $Re(SF_3)(CO)_4$, and $Re(F)(CO)_4$ structures.



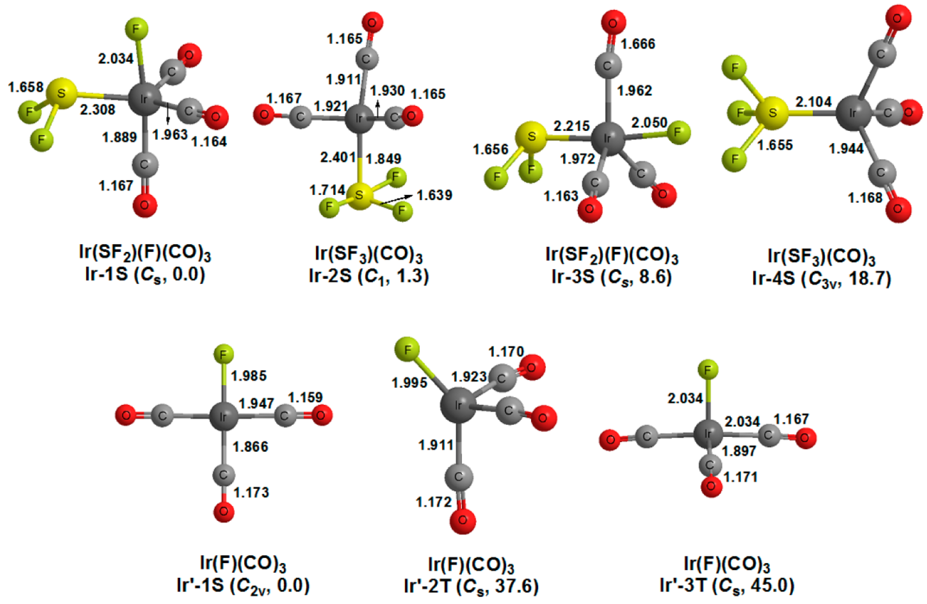
$CpOs(SF_2)(F)(CO)$
Os-1S (C_1, 0.0)

$CpOs(SF_2)(F)(CO)$
Os-2S (C_1, 0.7)

$CpOs(SF_3)(CO)$
Os-3S (C_s, 40.2)

$CpOs(F)(CO)$
Os'-1S (C_s, 0.0)

Figure 6. Optimized geometries for the $CpOs(SF_2)(F)(CO)$, $CpOs(SF_3)(CO)$, and $CpOs(F)(CO)$ structures.



$Ir(SF_2)(F)(CO)_3$
Ir-1S (C_s, 0.0)

$Ir(SF_3)(CO)_3$
Ir-2S (C_1, 1.3)

$Ir(SF_2)(F)(CO)_3$
Ir-3S (C_s, 8.6)

$Ir(SF_3)(CO)_3$
Ir-4S (C_{3v}, 18.7)

$Ir(F)(CO)_3$
Ir'-1S (C_{2v}, 0.0)

$Ir(F)(CO)_3$
Ir'-2T (C_s, 37.6)

$Ir(F)(CO)_3$
Ir'-3T (C_s, 45.0)

Figure 7. Optimized geometries for the $Ir(SF_2)(F)(CO)_3$, $Ir(SF_3)(CO)_3$, and $Ir(F)(CO)_3$ structures.

rhenium atoms in all three $Re(SF_2)(F)(CO)_4$ structures have the favored 18-electron configuration.

The isomeric $Re(SF_3)(CO)_4$ structure **Re-4S** is a very high energy structure, lying 44.0 kcal/mol in energy above **Re-1S** (Figure 5). The Re−S distance in **Re-4S** of 2.168 Å is significantly shorter than the ∼2.3−2.5 Å Re−S distances in **Re-nS** (**n** = 1, 2, 3). This suggests significantly stronger bonding between the SF_3 group and the Re atom in **Re-4S** relative to that in any of the $Re(SF_2)(F)(CO)_4$ structures.

The corresponding metal carbonyl fluoride $Re(F)(CO)_4$ structures were also studied to investigate the thermodynamic stability of the $Re(SF_2)(F)(CO)_4$ structures toward liberation of SF_2. Two Re(F)$(CO)_4$ structures were optimized (Figure 5). The global minimum **Re′-1S** has trigonal bipyramidal rhenium coordination with the fluorine atom in an equatorial position. The C_{4v} Re(F)$(CO)_4$ structure **Re′-2S** is a high energy structure, lying 36.7 kcal/mol above **Re′-1S**. Structure **Re′-2S** has square pyramidal Re coordination with the fluorine atom in the apical position and thus can be derived from **Re-3S** by removal of the SF_2 group. The predicted Re—F distances in the Re(F)$(CO)_4$ structures of ~2.0 Å are a little shorter than those in the Re(SF_2)(F)$(CO)_4$ structures.

3.4. CpOs(SF_2)(F)(CO) and CpOs(SF_3)(CO) Derivatives. The two CpOs(SF_2)(F)(CO) structures **Os-1S** and **Os-2S** have very similar geometries and energies, differing only in the orientations of the SF_2 group relative to the other ligands (Figure 6). Thus, structure **Os-2S** lies only 0.7 kcal/mol in energy above **Os-1S** implying a fluxional system. The singlet CpOs(SF_3)(CO) isomer **Os-3S** is a high energy structure, lying 40.2 kcal/mol above **Os-1S**. The SF_3 ligand in **Os-3S** is a three-electron donor with tetrahedral sulfur coordination thereby giving the osmium atom the favored 18-electron configuration.

The single structure **Os′-1S** found for the carbonyl fluoride CpOs(F)(CO) is a C_s structure with one terminal F atom, one terminal carbonyl group, and one terminal η^5-Cp ring (Figure 6). The Os—F distance in **Os′-1S** of ~1.94 Å is ~0.1 Å shorter than the Os—F distances in the CpOs(SF_2)(F)(CO) structures.

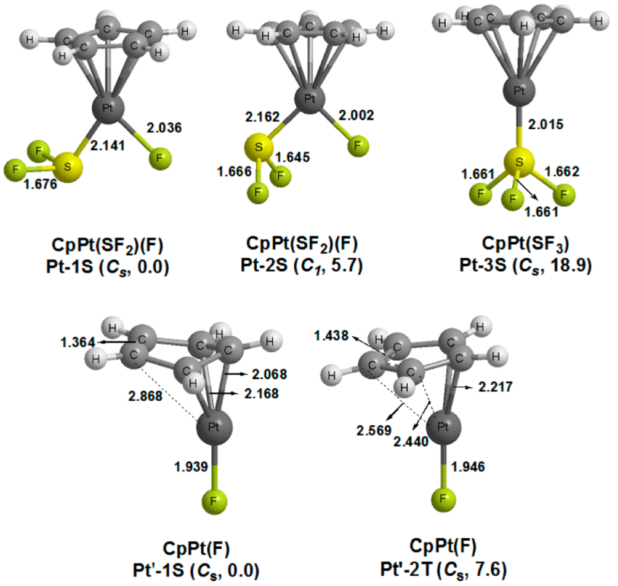
3.5. Ir(SF_3)$(CO)_3$ and Ir(SF_2)(F)$(CO)_3$ Derivatives. Two Ir(SF_2)(F)$(CO)_3$ structures and two Ir$(SF_3)(CO)_3$ structures were found (Figure 7). Unlike the other third row transition metals discussed in this Article or the first row transition metals discussed in the previous paper,[22] the lowest energy Ir(SF_2)(F)$(CO)_3$ and Ir$(SF_3)(CO)_3$ structures are very closely spaced in energy and thus may be regarded as essentially degenerate. For the Ir(SF_2)(F)$(CO)_3$, isomer **Ir-1S** with C_s symmetry is predicted to be the global minimum structure, and the Ir$(SF_3)(CO)_3$ structure **Ir-2S** lies only 1.3 kcal/mol above this global minimum.

The Ir(SF_2)(F)$(CO)_3$ structures **Ir-1S** and **Ir-3S** both exhibit approximate trigonal bipyramidal coordination of the central iridium atom (Figure 7). In **Ir-1S** the separate SF_2 and F ligands exhibit *cis* geometry occupying equatorial and axial positions, respectively, of the iridium trigonal bipyramid. Structure **Ir-3S**, lying 8.6 kcal/mol in energy above **Ir-1S**, has *trans* geometry of the SF_2 and F ligands, which are both located in the axial positions of the trigonal bipyramid. The Ir—F and Ir—S distances in **Ir-1S** and **Ir-3S** are ~2.0 and ~2.3 Å, respectively.

Two Ir$(SF_3)(CO)_3$ structures were found (Figure 7). The SF_3 group in the lower lying structure **Ir-2S** is only a one-electron donor, with a stereochemically active lone pair in one of the basal positions of a pseudo-square-pyramidal sulfur atom. Thus, the iridium atom in **Ir-2S** has only a 16-electron configuration rather than the favored 18-electron configuration. The SF_3 ligand in **Ir-2S** can be regarded formally as a monoanion so the iridium is in the formal Ir(I) oxidation state with a d^8 configuration. A 16-electron configuration for a d^8 transition metal such as Ir(I) in stable complexes is not unusual. The C_{3v} structure **Ir-4S**, lying 18.7 kcal/mol above **Ir-1S**, has a three-electron donor SF_3 group with tetrahedral sulfur coordination thereby giving the iridium atom the favored 18-electron configuration. The Ir—S distance in **Ir-4S** of 2.104 Å to the three-electron donor tetrahedral SF_3 ligand is considerably shorter than the 2.401 Å Ir—S distance to the one-electron donor pseudo-square-pyramidal SF_3 ligand in **Ir-2S**. This is consistent with a formal Ir≡S triple bond in **Ir-4S** but only an Ir—S single bond in **Ir-2S**.

One singlet and two triplet Ir(F)$(CO)_3$ structures were found (Figure 7). The global minimum **Ir′-1S** is a C_{2v} structure with approximate square planar iridium coordination. The triplet C_s structure **Ir′-2T** is a high energy structure, lying 37.6 kcal/mol above **Ir′-1S** with distorted tetrahedral iridium coordination. Structure **Ir′-2T** can be derived from the singlet Ir(SF_2)(F)$(CO)_3$ structure **Ir-1S** by removal of the SF_2 group. The C_s structure **Ir′-3T** is an even higher energy structure, lying 45.0 kcal/mol above **Ir′-1S**. Structure **Ir′-3T** can be derived from the singlet Ir(SF_2)(F)$(CO)_3$ structure **Ir-3S** by removal of the SF_2 group. The Ir—F distances in **Ir′-3T** are a little longer than those in **Ir′-1S** and **Ir′-2T**.

3.6. CpPt(SF_2)(F) and CpPt(SF_3) Derivatives. Two CpPt(SF_2)(F) structures and one CpPt(SF_3) structure were found (Figure 8). The CpPt(SF_2)(F) structure **Pt-2S** lies 5.7 kcal/mol in energy above **Pt-1S**. The main difference between **Pt-1S** and **Pt-2S** is the orientation of the SF_2 group. The CpPt(SF_3) structure **Pt-3S** lies 18.9 kcal/mol above **Pt-1S** (Figure 8). The Pt—S bond distance of 2.015 Å in the CpPt(SF_3) structure **Pt-3S** is significantly shorter than the Pt—S distance of ~2.15 Å in the CpPt(SF_2)(F) structures.



CpPt(SF_2)(F)
Pt-1S (C_s, 0.0)

CpPt(SF_2)(F)
Pt-2S (C_1, 5.7)

CpPt(SF_3)
Pt-3S (C_s, 18.9)

CpPt(F)
Pt'-1S (C_s, 0.0)

CpPt(F)
Pt'-2T (C_s, 7.6)

Figure 8. Optimized geometries for the CpPt(SF_2)(F), CpPt(SF_3), and CpPt(F) structures.

The lowest energy CpPt(F) structure **Pt′-1S** (Figure 8) is a C_s structure with a trihapto η^3-Cp ring and a Pt—F distance of 1.939 Å. The second CpPt(F) structure is a triplet state structure **Pt′-2T** lying 7.6 kcal/mol above **Pt′-1S** with a similar Pt—F distance. The Cp ring in **Pt′-2T** is a dihapto η^2-Cp rather than a trihapto or pentahapto ligand with three "non-bonding" Pt···C distances of more than ~2.4 Å.

3.7. Thermochemistry. Tables 1 and 2 list predicted energies for the isomerization reactions [M](SF_3) → [M](F)(SF_2) and the SF_2 elimination reactions [M](SF_2)(F) → [M](F) + SF_2, respectively. The conversions of the [M](SF_3) derivatives ([M] = Ta$(CO)_5$, CpW$(CO)_2$, Re$(CO)_4$, CpOs(CO), Ir$(CO)_3$, and CpPt) to the corresponding isomeric [M](SF_2)(F) derivatives are predicted to be exothermic, with the heat of this reaction increasing in the sequence Ir(SF_3)-

Table 1. Isomerization Energies (kcal/mol) for $[M](SF_3) \rightarrow [M](SF_2)(F)$ Based on the Lowest Energy Structures

$[M](SF_3) \rightarrow [M](SF_2)(F)$	ΔE BP86
$Ta(SF_3)(CO)_5 \rightarrow Ta(SF_2)(F)CO)_5$	−32.3
$CpW(SF_3)(CO)_2 \rightarrow CpW(SF_2)(F)(CO)_2$	−26.0
$Re(SF_3)(CO)_4 \rightarrow Re(SF_2)(F)(CO)_4$	−44.0
$CpOs(SF_3)(CO) \rightarrow CpOs(SF_2)(F)(CO)$	−40.2
$Ir(SF_3)(CO)_3 \rightarrow Ir(SF_2)(F)(CO)_3$	−1.3
$CpPt(SF_3) \rightarrow CpPt(SF_2)(F)$	−18.9

Table 2. SF_2 Dissociation Energies (kcal/mol) for $[M](SF_2)(F) \rightarrow [M](F) + SF_2$ Based on the Lowest Energy Structures

$[M](SF_2)(F) \rightarrow [M](F) + SF_2$	ΔE BP86
$Ta(SF_2)(F)CO)_5 \rightarrow Ta(F)(CO)_5 + SF_2$	15.0
$CpW(SF_2)(F)(CO)_2 \rightarrow CpW(F)(CO)_2 + SF_2$	29.3
$Re(SF_2)(F)(CO)_4 \rightarrow Re(F)(CO)_4 + SF_2$	22.0
$CpOs(SF_2)(F)(CO) \rightarrow CpOs(F)(CO) + SF_2$	36.5
$Ir(SF_2)(F)(CO)_3 \rightarrow Ir(F)(CO)_3 + SF_2$	10.8
$CpPt(SF_2)(F) \rightarrow CpPt(F) + SF_2$	37.9

$(CO)_3 \ll CpPt(SF_3) < CpW(SF_3)(CO)_2 < Ta(SF_3)(CO)_5 < CpOs(SF_3)(CO) < Re(SF_3)(CO)_4$. However, the isomerization of the lowest energy $Ir(SF_3)(CO)_3$ structure is within ~1.5 kcal/mol of being thermoneutral so that it might be a marginally viable species. The isomerization energies of the other $[M](SF_3)$ complexes are substantial ranging from 18.9 kcal/mol for $CpPt(SF_3) \rightarrow CpPt(SF_2)(F)$ to 44.0 kcal/mol for $Re(SF_3)(CO)_4 \rightarrow Re(SF_2)(F)(CO)_4$. Thus, these $[M](SF_3)$ complexes do not appear to be viable.

The corresponding metal carbonyl fluoride structures $[M](F)$ were studied to determine the SF_2 dissociation energies of the $[M](SF_2)(F)$ complexes (Table 2). All of the $[M](SF_2)(F)$ complexes are seen to be viable toward SF2 dissociation. This suggests SF_2 metal complexes to be viable synthetic objectives if methods can be found to circumvent the use of the unstable SF_2 as a source of the SF_2 ligand.

3.8. Vibrational Frequencies. Table 3 shows the vibrational frequencies in the trifluorosulfane metal complexes obtained by the BP86 method without any scaling factors. The structures with three-electron donor SF_3 groups with a tetrahedrally coordinated central sulfur atom exhibit three $\nu(SF)$ frequencies in a ~300 cm^{-1} range with the lowest $\nu(SF)$ frequency at 484−646 cm^{-1}. The pattern is different with the single example of a trifluorosulfane metal complex having a one-electron donor SF_3 group with a pseudo-squar- pyramidal sulfur atom (Figure 2), namely the $Ir(SF_3)(CO)_3$ structure **Ir-2S** in which the lowest $\nu(SF)$ frequency is 379 cm^{-1} and the three $\nu(SF)$ frequencies span a range of ~350 cm^{-1}. This difference may be a consequence of the two fluorine atoms in *trans* positions in pseudo-square-pyramidal SF_3 coordination. This suggests that the pattern of $\nu(SF)$ frequencies might distinguish between three-electron donor SF_3 groups with tetrahedral sulfur atoms and one-electron donor SF_3 groups with pseudo-tetragonal-pyramidal sulfur atoms.

Table 4 shows the harmonic vibrational frequencies for the $[M](SF_2)(F)$ derivatives. The terminal $\nu(MF)$ frequencies fall in the rather narrow range 492−538 cm^{-1}. The $\nu(MF)$ frequency in the $Re(F)(SF_2)(CO)_4$ structure **Re-1S** for the fluorine atom bridging the Re−S bond is distinctly lower at 441 cm^{-1}. The SF_2 ligands in the $[M](SF_2)(F)$ derivatives exhibits a pair of $\nu(SF)$ frequencies in the 546−740 cm^{-1} range. The singlet metal fluoride derivatives $[M](F)$ exhibit a single $\nu(MF)$ frequency ranging from 539 to 598 cm^{-1} (Table 5). The triplet metal fluoride derivatives exhibit lower $\nu(MF)$ frequencies ranging from 470 to 566 cm^{-1}.

Table 4. Harmonic Vibrational Frequencies (in cm^{-1}) for the $[M](SF_2)(F)$ Derivatives

	$\nu(CO)$	$\nu(MF)$	$\nu(SF)$
	$Ta(SF_2)(F)(CO)_5$		
Ta-1S (C_1)	1931(631), 1947(862), 1988(1541), 1998(654), 2059(284)	529(48)	681(152), 697(295)
Ta-2S (C_1)	1977(936), 1984(1501), 1989(980), 2003(488), 2069(209)	520(96)	597(48), 627(321)
	$CpW(SF_2)(F)(CO)_2$		
W-1S (C_1)	1996(780), 1948(764)	497(19)	596(116), 658(308)
W-2S (C_s)	1952(1209), 2002(430)	538(83)	546(60), 600(296),
	$Re(SF_2)(F)(CO)_4$		
Re-1S (C_1)	1978(941), 2002(1293), 2010(731), 2093(139)	441(48)	702(206), 740(145)
Re-2S (C_s)	1964(879), 2015(1525), 2024(598), 2097(179)	503(52)	710(287), 713(90)
Re-3S (C_s)	2008(1536), 2027(1464), 2054(50), 2112(98)	492(86)	613(105), 633(291)
	$CpOs(SF_2)(F)(CO)$		
Os-1S (C_1)	2005(703)	515(34)	611(123) ,663(350)
Os-2S (C_1)	1986(789)	515(25)	606(150) ,650(265)
	$Ir(SF_2)(F)(CO)_3$		
Ir-1S (C_s)	2022(964), 2026(637), 2083(346)	511(25)	665(116), 705(275)
Ir-3S (C_s)	2019(643), 2022(1001), 2079(357)	527(54)	699(106), 728(244)
	$CpPt(SF_2)(F)$		
Pt-1S (C_s)		497(38)	672(355), 604(108)
Pt-2S (C_1)		517(48)	654(218), 711(334)

Table 3. Harmonic Vibrational Frequencies (in cm^{-1}) for the $[M](SF_3)$ Derivatives

structures		ν (CO)	ν (SF)
$Ta(SF_3)(CO)_5$	**Ta-3S** (C_s)	1967(1850), 1967(1862), 1976(8), 2006(495), 2058(450)	619(92), 621(92), 743(952)
$CpW(SF_3)(CO)_2$	**W-3S** (C_s)	1941(958), 1989(687)	603(108),630(159), 772(674)
$Re(SF_3)(CO)_4$	**Re-4S** (C_s)	1980(1195), 2002(263), 2011(1412), 2081(220)	590(182), 678(137), 746(834)
$CpOs(SF_3)(CO)$	**Os-3S** (C_s)	1988(745)	484(6), 570(168), 687(162)
$Ir(SF_3)(CO)_3$	**Ir-2S** (C_1)	2018(1144), 2034(519), 2094(263)	379(5), 635(295), 737(118)
	Ir-4S (C_{3v})	2011(875), 2011(875), 2060(343)	646(177), 646(177), 773(812)
$CpPt(SF_3)$	**Pt-3S** (C_s)		488(14), 622(144), 622(143)

Table 5. Harmonic Vibrational Frequencies (in cm^{-1}) for the [M](F) Derivatives

structures	ν(CO)	ν(MF)
	$Ta(F)(CO)_5$	
Ta′-1S (C_s)	1931(1495), 1941(292), 1955(688), 1986(1736), 2061(35)	567(77)
Ta′-2T (C_{4v})	1942(699), 1960(1980), 1960(1980), 1979(0), 2060(26)	566(85)
	$CpW(F)(CO)_2$	
W′-1S (C_s)	1950(769), 1875(868)	598(63)
W′-2S (C_s)	1862(1740), 1942(479)	582(65)
	$Re(F)(CO)_4$	
Re′-1S (C_{2v})	1963(1024), 1984(522), 2001(1648), 2094(13)	553(67)
Re′-2S (C_{4v})	1963(2012), 1963(2012), 2014(0), 2084(8)	539(44)
	$CpOs(F)(CO)$	
Os′-1S (C_s)	1954(857)	571(69)
	$Ir(F)(CO)_3$	
Ir′-1S (C_{2v})	2019(663), 2044(1414), 2136(8)	547(54)
Ir′-2T (C_s)	1981(903), 1984(919), 2032(250)	517(12)
Ir′-3T (C_s)	1989(1463), 1997(755), 2060(32)	470(36)
	$CpPt(F)$	
Pt′-1S (C_s)		573(90)
Pt′-2T (C_s)		563(93)

3.9. Natural Bond Orbital (NBO) Analysis.

Table 6 reports the distances and Wiberg bond indices (WBIs) for the metal−sulfur bonds in the metal SF_3 complexes reported in this Article using natural bond orbital (NBO) analyses.[36−38] In connection with the interpretation of the WBIs, metal−metal bonds involving transition metals have been shown generally to have WBIs of only a fraction of the assigned formal bond orders. However, the relative values of WBIs of transition metal−metal bonds are consistent with the formal bond orders as inferred from metal−metal distances, electron counting, etc. For the M≡S bonds in the metal SF_3 complexes with tetrahedral SF_3 ligands corresponding to neutral three-electron donors (Figure 2), the WBIs range from 1.4 to 1.7 consistent with metal−sulfur formal triple bonds. However, for the Ir—S bond in the $Ir(SF_3)(CO)_3$ complex **Ir-2S** with a pseudo-square-pyramidal SF_3 ligand corresponding to a neutral one-electron donor, the WBI is much lower at ∼0.7. This is consistent with a formal Ir—S single bond, possibly with some additional backbonding from the iridium atom into antibonding orbitals of the SF_3 ligand.

Table 6. Wiberg Bond Indices (WBI) of the Metal−Sulfur Bonds in the $[M]SF_3$ from NBO Analysis

		M−S		
BP86		bond length (Å)	formal bond order	WBI
$Ta(SF_3)(CO)_5$	**Ta-3S** (C_s)	2.273	3	1.50
$CpW(SF_3)(CO)_2$	**W-3S** (C_s)	2.151	3	1.68
$Re(SF_3)(CO)_4$	**Re-4S** (C_s)	2.168	3	1.44
$CpOs(SF_3)(CO)$	**Os-3S** (C_s)	2.073	3	1.53
$Ir(SF_3)(CO)_3$	**Ir-4S** (C_{3v})	2.104	3	1.50
$Ir(SF_3)(CO)_3$	**Ir-2S** (C_1)	2.401	1	0.70
$CpPt(SF_3)$	**Pt-3S** (C_s)	2.015	3	1.44

4. CONCLUSIONS

This theoretical study predicts that the trifluorosulfane metal complexes $[M]SF_3$ ($[M] = Ta(CO)_5$, $Re(CO)_4$, $CpW(CO)_2$, $CpOs(CO)$, and $CpPt$) are clearly thermodynamically disfavored relative to the isomeric $[M](SF_2)(F)$ derivatives. Thus, the reactions $[M](SF_3) \rightarrow [M](SF_2)(F)$ become increasingly exothermic in the sequence $CpPt(SF_3) < CpW(SF_3)(CO)_2 < Ta(SF_3)(CO)_5 < CpOs(SF_3)(CO) < Re(SF_3)(CO)_4$ with energies ranging from 18.9 to 44.0 kcal/mol. This energy sequence is similar to that previously found for the first row transition metals except for the position of $CpPt(SF_3)$. However, these reactions for the third row transition metals are less exothermic than the corresponding reactions for the first row transition metals.[22]

The iridium derivative $Ir(SF_3)(CO)_3$ (**Ir-2S** in Figure 7) is anomalous since the predicted energy for the fluorine transfer from sulfur to iridium to give $Ir(SF_2)(F)(CO)_3$ is essentially thermoneutral within ∼1.5 kcal/mol (Table 1). A close examination of the **Ir-2S** structure indicates pseudo-square-pyramidal rather than tetrahedral geometry of the SF_3 ligand (Figure 2). This indicates that the SF_3 ligand in the $Ir(SF_3)(CO)_3$ structure **Ir-2S** is a one-electron donor thereby giving the iridium atom a 16-electron configuration. Considering the one-electron donor pseudo-square-pyramidal SF_3 ligand as a monoanion gives the iridium atom a formal +1 oxidation state with a d^8 configuration. Stable square planar complexes with 16-electron configurations for the central metal atom are commonly encountered with d^8 transition metals, particularly those in the second and third rows. The Ir—S distance of 2.401 Å in the $Ir(SF_3)(CO)_3$ structure **Ir-2S** with a one-electron donor pseudo-square-pyramidal SF_3 ligand is significantly longer than the 2.01 to 2.27 Å M≡S distances found in the other $[M](SF_3)$ complexes with tetrahedral three-electron donor SF_3 groups. This is consistent with a formal M≡S triple bond of transition metals to tetrahedral SF_3 groups similar to the N≡S triple bond in $N{\equiv}SF_3$.[39,40] The presence of formal M≡S triple bonds in the $[M](SF_3)$ complexes with tetrahedral $[M]SF_3$ geometry is also supported by relatively high Wiberg bond indices for the M≡S bonds ranging from 1.4 to 1.7 (Table 6).

The anomalous resistance of $Ir(SF_3)(CO)_3$ toward fluorine shift from sulfur to the metal suggests that the best chances of obtaining viable metal SF_3 complexes use systems in which the SF_3 ligand is forced to be a one-electron donor pseudo-square-pyramidal ligand rather than a three-electron donor tetrahedral ligand. Note that the one known example of an experimentally realized stable SF_3 complex, namely $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$,[17] is also an iridium complex having a one-electron donor pseudo-square-pyramidal SF_3 ligand (Figure 2) similar to the anomalously marginally viable $Ir(SF_3)(CO)_3$ (**Ir-2S**). In addition, a much higher energy $Ir(SF_3)(CO)_3$ structure **Ir-4S**, lying 18.7 kcal/mol in energy above the lowest energy $Ir(F)(SF_2)(CO)_3$ structure **Ir-1S**, was found with a tetrahedral three-electron donor SF_3 ligand. The Ir−S distance of 2.104 Å in **Ir-4S** with a three-electron donor SF_3 ligand is ∼0.3 Å shorter than the Ir−S distance of 2.401 Å in **Ir-2S** with a one-electron donor SF_3 ligand. This is consistent with a three-electron donor tetrahedral SF_3 ligand forming a multiple bond with the metal atom but a one-electron donor pseudo-square-pyramidal SF_3 ligand forming only a single bond with the metal atom.

The fluorine shift reactions $[M](SF_3) \rightarrow [M](SF_2)(F)$ suggest synthetic approaches to metal complexes of difluorosulfane (SF_2) using the known SF_3^+ cation[15,16] as a source of SF_2. Such a synthetic approach circumvents the need for the unstable SF_2 as a reagent for the synthesis of such complexes.

The viability of the metal SF_2 complexes was examined by predicting the energies for the SF_2 dissociation reactions $[M](SF_2)(F) \rightarrow [M](F) + SF_2$. All such reactions were found to become increasingly endothermic in the sequence $Ir(SF_2)(F)(CO)_3 \ll Ta(SF_2)(F)(CO)_5 < Re(SF_2)(F)(CO)_4 < CpW(SF_2)(F)(CO)_2 < CpOs(SF_2)(F)(CO) < CpPt(SF_2)(F)$ with predicted energies ranging from ~11 to ~38 kcal/mol. The anomalously low dissociation energy of the 18-electron complex $Ir(SF_2)(F)(CO)_3$ to give the 16-electron complex $Ir(F)(CO)_3 + SF_2$ is a consequence of the favorable stability of square planar 16-electron complexes of d^8 transition metals such as Ir(I) in $Ir(F)(CO)_3$. In addition, substituting CO groups with the weaker π-accepting Cp ligand increases the back-bonding to the SF_2 ligand and thus the energy required for dissociation of the SF_2 ligand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables S1−S5 showing coordinates of the Ta sulfur fluoride derivatives; Tables S6−S10 showing coordinates of the W sulfur fluoride derivatives; Tables S11−S16 showing coordinates of the Re sulfur fluoride derivatives; Tables S17−S20 showing coordinates of the Os sulfur fluoride derivatives; Tables S21−S27 showing coordinates of the Ir sulfur fluoride derivatives; Tables S28−S32 showing coordinates of the Pt sulfur fluoride derivatives; Tables S33−S38 showing harmonic vibrational frequencies of the Ta, W, Re, Os, Ir, Pt sulfur fluoride derivatives; Figures S1−S6 showing optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the Ta, W, Re, Os, Ir, Pt sulfur fluoride derivatives; Tables S39−S44 showing total energies (E, in hartree), relative energies (ΔE, in kcal/mol), and numbers of imaginary vibrational frequencies (Nimag) for the Ta, W, Re, Os, Ir, Pt sulfur fluoride derivatives; Table S45 showing the isomerization energies (kcal/mol) for $[M](SF_3) \rightarrow [M](SF_2)(F)$ based on the lowest energy structures by the BP86 and B3LYP methods; Table S46 showing SF_2 dissociation energies (kcal/mol) for $[M](SF_2)(F) \rightarrow [M](F) + SF_2$ based on the lowest energy structures by the BP86 and B3LYP methods; complete Gaussian reference. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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